

## VERY HIGH FREQUENCY EPR SPECTROSCOPY AND NMR IMAGING OF COAL

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### INTRODUCTION

Last year we began a program to develop and apply Very High Frequency Electron Paramagnetic Resonance (VHF EPR) to non-destructively analyze for organic sulfur molecular forms in coal and separated macerals. The starting point of our work was a preliminary observation that when EPR spectra of coal were taken on our newly constructed VHF spectrometer [1], signals related to organic sulfur were observable. These spectral features could only be resolved at high magnetic fields, and hence had gone undetected in all previous EPR studies of coal, although their presence had been inferred from indirect evidence [2]. Figure 1 clearly shows the resolution of sulfur-related features in an Illinois #6 whole coal at 96 GHz. We also began to develop magnetic resonance imaging techniques to non-destructively assess the effects of various solvents on coal, including the measurement of solvent swelling and solvent penetration. In this report we will discuss recent progress made in both of these areas.

### VHF EPR ANALYSIS

What makes the discovery of sulfur-related peaks in the VHF EPR spectra of coal useful as well as interesting is the fact that spectra like that shown in Fig. 1 have the potential to be understood theoretically, thus allowing for the development of a technique which can be analytical for organic sulfur in coal. Furthermore, information from organic sulfur model compounds like dibenzothiophene and benzonaphthothiophene, shown in Figure 2, allow theory to be tested on ideal molecular systems with properties thought to be very similar to those of whole coal. We have developed chemical techniques to synthesize stable cation radical forms of such coal model sulfur compounds, utilizing either (i) boric acid glass matrix isolation followed by UV irradiation, or (ii) formation by electron transfer on catalytically active silica-alumina surfaces [3]. Spectra from compounds such as these form the basis of our interpretation of the more complex spectra obtained from coal.

Three examples will be given to illustrate some of the potential in the VHF EPR method, and the rationale of our approach. The first, shown in Figure 3, compares the VHF EPR spectra of vitrinite and sporinite macerals separated from an Illinois #6. Careful destructive chemical analysis suggests that the vitrinite contains 2.9% organic sulfur, while the sporinite contains 4.3%. Analysis of the VHF EPR spectra of these two samples on the basis of a two-species model, involving the summation of spectra from sulfur and non-sulfur containing species indicates almost identical sulfur levels as obtained by chemical analysis [4]. While the two-species model seems crude, it has proven to be quite useful in analyzing VHF EPR coal spectra, and may represent a reasonable generalization regarding the classes of organic molecular forms contributing to the spectral lineshape. We suggest that at 96 GHz, spin-orbit coupling between unpaired electrons and aromatic sulfur produces the downfield shifts which we resolve in spectra from high-sulfur coal; similar SO coupling effects from oxygen species produce shifts too small to be resolved at this frequency. In collaboration with Prof. Jack Freed (Cornell University), we have examined samples at 250 GHz, and there see lineshapes which may allow a more detailed analysis of

heteratom (S,O) effects.

Figure 4 compares two "before and after" samples in order to study the effects of two desulfurization methods on an Illinois #6. In Figure 4(a), the coal was subjected to extraction with perchloroethylene (PCE) at 120°C for 3.5 hours. As can be seen by inspection, very little changed in the VHF EPR spectra as a result of this treatment, suggesting that little organic sulfur (of the aromatic variety to which our method is believed to be sensitive) was removed, in agreement with D. H. Buchanan and co-workers, from whom the samples were obtained [5]. Figure 4(b) shows spectra of the Illinois #6 before and after low temperature (285°C) pyrolysis for two hours under vacuum conditions ( $P < 10^{-5}$  Torr). The greatly reduced low-field peak ( $g = 2.00434$ ) in the pyrolyzed coal suggests that this treatment significantly altered and removed aromatic organic sulfur, as has been reported by Kruse and Shimp [6]. We currently are employing VHF EPR to study the effects of low-temperature pyrolysis on coal structure, and have observed complex spectral changes which need to be understood before a complete interpretation of these effects can be made.

Figure 5. shows VHF EPR spectra of the two model compounds in Figure 2. One primary difference between DBT and BNT is that DBT contains 12 aromatic carbons, while BNT contains 16. As the figure illustrates, this difference of four atoms has a large effect on the spectral lineshape. One component of this sensitivity of lineshape to aromatic ring size is that the g-anisotropy brought about by spin-orbit interactions ( $\lambda L \cdot S$ ) depends strongly on the unpaired electron spin density on sulfur. As aromatic ring size increases and the unpaired electron delocalizes over a larger carbon skeleton, density on sulfur decreases, resulting in diminished anisotropy, which agrees with the changes seen in the spectra of Fig. 5. We currently are studying a series of thiophenic compounds with varying aromatic ring sizes, in order to develop this theory further.

## NMR IMAGING OF SOLVENTS IN COAL

Nuclear magnetic resonance imaging (MRI) can be used in a completely non-invasive way to visualize and measure the changes in pore size as coal is swollen with organic solvents. Preliminary experiments have been carried out using two separate radiofrequency and gradient coil configurations in order to determine the feasibility of studying solvent diffusion into coal samples. The imaging system used is the SISCO 200/330 imaging spectrometer system, located in the Biomedical Magnetic Resonance Laboratory at the University of Illinois/Urbana. This instrument operates at a field strength of 4.7T ( $\nu(\text{proton}) = 200$  MHz). The first approach used the system's 8 cm. inner diameter double saddle radiofrequency probe as the transmit and receive coil, with the system's magnetic field gradients being driven by Oxford gradient amplifiers to give a maximum gradient strength of 2 G/cm. Additional work now is being carried out using an imaging probe from Doty Scientific, consisting of a solenoidal radiofrequency probe of inner diameter 1.5 cm., and maximum gradient strength of 15 G/cm., when driven by three Techron power supplies.

Samples were obtained from the Illinois State Geological Survey. First, the coal sample was immersed in water, doped with manganese chloride, in order to reduce solvent proton  $T_1$  to 400 msec, and allowed to soak for a week. MRI images then were taken. The water then was removed, and the sample was placed in acetone, doped with 10 mM chromium acetoacetonate (AcAc) in order to reduce solvent proton  $T_1$  to 400 msec. After 48 hours of immersion, the sample was again imaged. Lastly, the acetone was removed, and the sample was immersed in DMSO, again doped with chromium AcAc. After another 48 hours of soaking, a third set of images were obtained.

Figure 6. shows a series of five images from a multislice data set obtained on a sample of Illinois #5 coal (Galatin County, IL), with dimensions of 19 x 19 x 38 mm. Since coal is not swollen by the water, these images define the outer surface of the pre-swollen coal, providing a

reference for subsequent swelling experiments. Each image represents a slice through the coal sample with an in-plane thickness of 1 mm. In plane spatial resolution is 500 microns.

Figure 7, shows the same coal sample after immersion in doped acetone. Some swelling and permeation of the solvent into the coal sample is clearly seen, although the covalent cross-linking in the coal is not yet being substantially broken. Figure 8, follows the same sample after 48 hours of immersion in doped DMSO. The images clearly show significant pore enlargement and swelling of the coal. It should be remembered that these images are internal views of the solid sample, permitting non-destructive analysis, and hence sequential solvent studies on the same piece of coal.

MRI results agree qualitatively with those obtained using methods where no spatial localization or visualization was possible. Estimates of the swelling ratio,  $Q$ , for our coal sample in DMSO and acetone, made from the images in Figs. 7 and 8, yield a value of 1.9. Szeliga and Marzec obtained a value of  $Q = 1.6$  for these solvents in a similar coal [7]. These authors have shown that swelling and solvent electron-donor number (defined as the negative of the enthalpy change for the interaction of the solvent with  $SbCl_5$  in a dilute solution of dichloroethane) show a reasonably strong correlation, and they discuss the solvents used in our MRI work. Brenner has shown that initial swelling is rapid, although weeks or even months may be necessary to reach equilibrium swelling [8]. He concluded that access of solvent to the sites where swelling is induced is highly variable: some pathways are accessible to the solvent molecules in seconds, others may take days. In the future, we hope to further develop MRI methods to follow these processes in greater detail.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

1. R. B. Clarkson, W. Wang, M. J. Nilges, and R. L. Belford, in *Processing and Utilization of High-Sulfur Coals III*, R. Markuszewski and T. D. Wheelock, eds, Elsevier, Amsterdam, 1990, pp. 67 - 78.
2. H. L. Retcofsky, M. R. Hough, M. M. Maguire, and R. B. Clarkson, in *Coal Structure*, M. L. Gorbaty and K. Ouchi, eds., ACS Advances in Chemistry No. 192, 1981, 37 - 58.
3. R. B. Clarkson, R. L. Belford, K. S. Rothenberger, and H. C. Crookham, *J. Catalysis*, 1987, **106**, 500.
4. R. B. Clarkson, W. Wang, D. R. Brown, H. C. Crookham, and R. L. Belford, *FUEL*, 1990, **69**, 1405.
5. D. H. Buchanan, K. J. Coombs, C. Chaven, C. W. Kruse, and K. C. Hackley, in *Processing and Utilization of High-Sulfur Coals III*, R. Markuszewski and T. D. Wheelock, eds., Elsevier, Amsterdam, 1990, pp. 79 - 87.
6. C. W. Kruse and N. E. Shimp, in *Coal Processing Technology*, v. VII, AlChE., 1981, 124.
7. J. Szeliga and A. Marzec, *FUEL*, 1983, **62**, 1229.
8. D. Brenner, Am. Chem. Soc. Div. Fuel Chem. Preprints, 1982, **27**, 244.

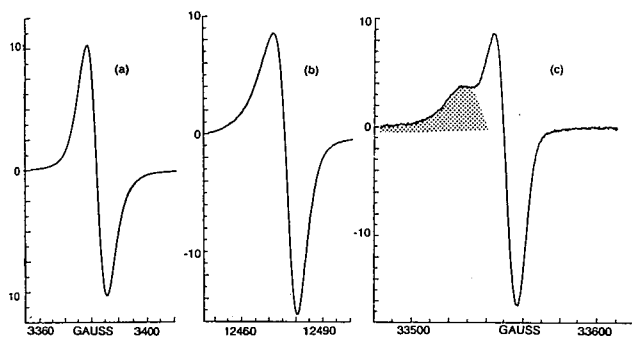


Figure 1. First evidence that VHF EPR can resolve sulfur-related spectral features in coal. (a) 9.5 GHz, (b) 35 GHz, (c) 96 GHz. Shaded area is the sulfur-related region.

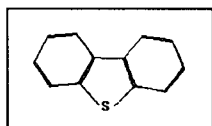


Figure 2. Dibenzothiophene, DBT, (l), and benzonaphthothiophene, BNT, (r).

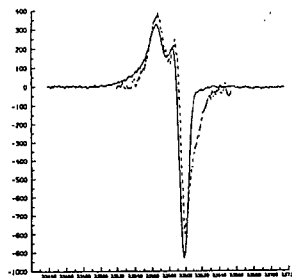
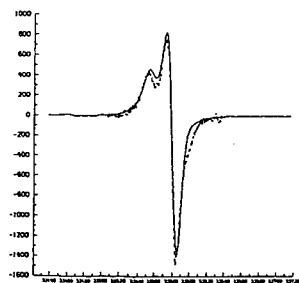
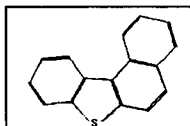


Figure 3. (a) Vitrinite, 2.9% organic S; (b) Sporinite, 4.3% organic S.

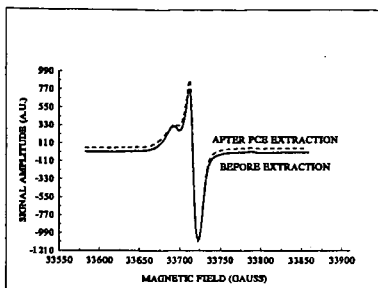


Figure 4(a). VHF EPR spectra of an Illinois #6 before (—) and after (---) PCE extraction.

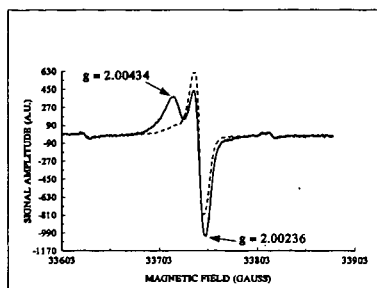


Figure 4(b). Illinois #6 coal before (—) and after (---) low temperature pyrolysis.

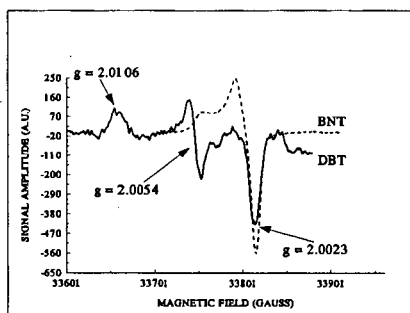


Figure 5. VHF EPR (ca. 96 GHz) spectra of DBT+ and BNT+ in boric acid glass.

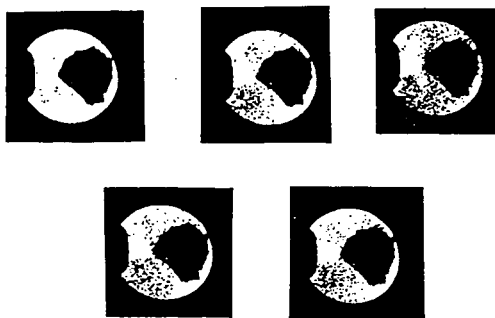


Figure 6. MRI images corresponding to five 1 mm. thick slices through an Illinois #5. Since water does not swell coal, this experiment defines the outer surface of the coal sample.



Figure 7. Same sample as in Fig. 6, but with acetone now as the solvent. A small degree of diffusion and swelling is observed.



Figure 8. Same sample, now with DMSO as the solvent. Pore enlargement and swelling are now clearly visible.